3013 Monitoring and Surveillance Shelf Life Studies

Quarterly Meeting
February 25-26, 2003
Savannah River Site
Room 1047, Building 766-H

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Problem

- DOE is planning to store Pu-bearing materials for 50 years that are stabilized and packaged to the 3013 storage standard.
- Storage requirements include a set of nested, welded, stainless steel containers.
- Past experience with PuO_2 materials has shown that gases may accumulate.
- The generation of H_2 or H_2O gases (pressurization) and HCl or Cl_2 gases (stress corrosion cracking) are of concern.

John Berg, David Harradine, Dallas Hill, Scott Lillard, Jim McFarlan, John Morris, Dennis Padilla, Coyne Prenge Kirk Veirs, Laura Worl   Los Alamos National Laboratory, *contact lworl@lanl.gov, 505-665-7149*

Full-Scale Study

Establish baseline behavior of full- scale containers and bound the behavior of material in extreme cases.

- 5 kg of oxide material in 9 sealed 3013 BNFL inner containers - 2.38 L

Continue radiography on sealed 3013-94 containers equipped with bellows.

- Pure Pu oxide material in 7 sealed containers (little moisture).

Small Scale Sample Study

Small 10 g samples allow a database of DOE material types prepared for storage in a variety of ways (material, temperature, moisture, fill gas,) to be compiled.

- Site-wide representative oxide samples prepared to DOE Standard; sample duplication; surveillance model failures

Large Scale Surveillance Test Results

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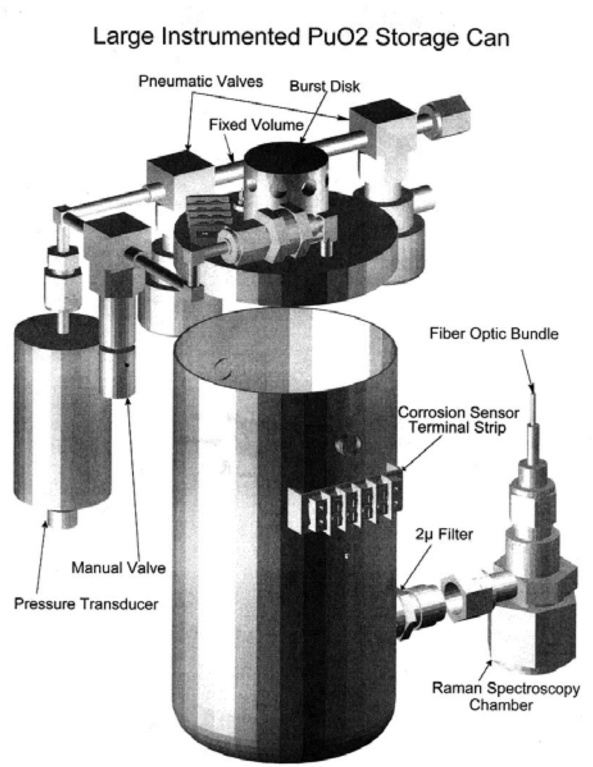

Large Scale Instrumented Surveillance Container 2300 cc.

Raman spectroscopy, gas chromatography, mass spec., temperature, pressure, acoustic resonance spectroscopy, general corrosion sensor monitoring

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Monitoring system for PuO_2 containers

- Gas samples drawn for analysis by GC and mass spec.
- Raman spectra can be taken inside the container.
- All instrumentation is outside of the glovebox line.
- Pressure and temperature continuously monitored.

Quality control procedures generate defensible data

- Quality Management Plan interfaces project with appropriate requirements
- Equipment calibrations are maintained
- Data Quality Plan specifies measurables and associated errors that are acceptable
- Experimental blanks are included
- After oxide is received, multiple tasks occur before container is installed on surveillance rack (lid weld, SNM verification, leak test at 1000 Torr for 4 days)
- Gas sampling and analysis are completed on specified schedule

Surveillance Glove box

gas chromatography, mass spectrometer, Raman spectroscopy, corrosion monitoring, pressure and temperature monitoring

Oxide Can 1

Blank Can

Large-scale Materials

CAN	MATERIAL[a,b]	Conditions	Fill Gas
1	**Pure PuO_2[c]**	Baseline 3013 Standard - calcined at 950°C, final SA<5 m^2/g, Dry	He
2	**Pure PuO_2, 25 gms H_2O[d], 0.5%**	"As Received," prior to final calcination, SA > 10 m^2/g	He
3	**Same as 1 and 100 gms H_2O, 2% cap**	Baseline 3013 Standard, final SA<5 m^2/g, exposed to humid gas	He
4	**34% PuO_2 + 33%$MgCl_2$ + 33%$CaCl_2$ salt**	Blend then 600°C calcination	air [e]
5	**PuO_2 + 5% organics**	Blend then 600°C calcination	He
6	**PuO_2 + 5% organics**	Blend then 600°C calcination	air
7	**Same as 1, 10 gms H_2O, 0.1% cap**	External heat - 210°C max. in headspace	He
8	**34% PuO_2 + 33%$MgCl_2$ + 33%$CaCl_2$ salt then 2% H_2O added**	Blend then calcined at 950°C, exposed to humid gas	air
9	**20 % Pu / 50% U**	Calcined at 950°C, final SA<5 m^2/g, H_20<0.5%	He

a) All % by weight. b) Container will be filled with 5 kg oxide or to fill line dependent on density. c) 84 - 88 wt% Pu. d) Water is added to the material by exposure of the oxide filled container to 60 % humid gas for a period of time. Water uptake is monitored by container weight gain. e) ARS in air containers.

Oxide Material for First Large Scale Container

Can 1, Baseline preparation 10/16/01- Simon Balkey

- **Four lots of PuO_2 were combined (5496.3 g), screened, V-blended (1 hr), calcined - (975 ^{0}C for 4 hrs), screened and blended again. Grab sample (~450g) pulled for MIS.**

- **Plutonium Isotopics**

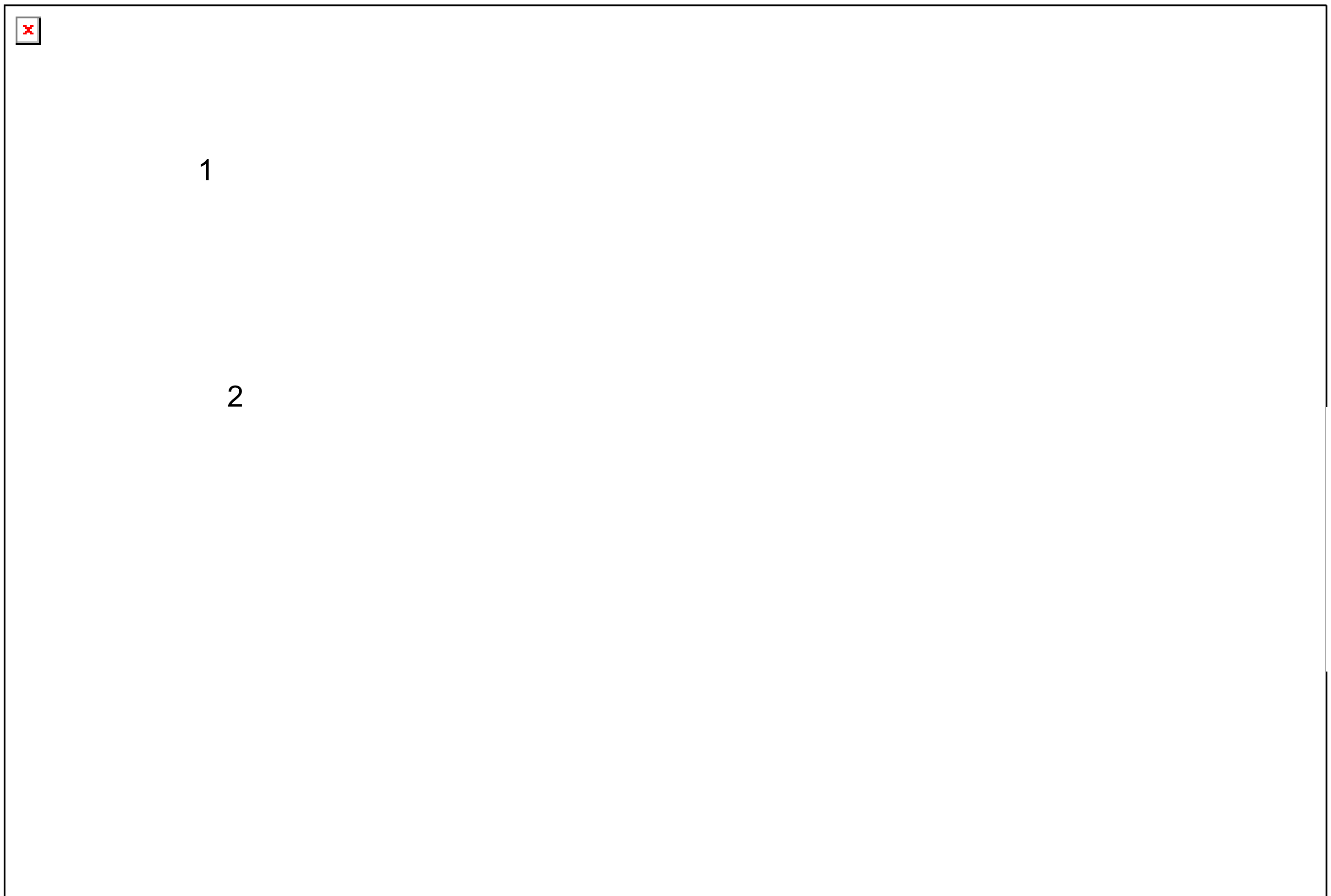
Pu^{239} 93.7%
Pu^{240} 6.1%
Pu^{241} 0.15%
Pu^{242} 0.03%
Pu^{238} 0.02%

**Impurities > 20 ppm*

Can 1 Oxide - R200145 *		
Calcined at 975C, 4 hours	**Value**	**Units**
Date Calcined	10/17/05	Date
Date of Oxide Prep (oxalate ppt)	6/00	Date
Net Mass lost in Calcination	45.8	g
LOI (average)	0.1	wt. %
H2O (Interstital gas analysis)	0.07	wt. %
Particle size (spherical eq. mean)	21.8	microns
Density - pycnometer	11.4	g/cm^3
Specific Surface Area	1.09	m^2/g
Wattage	10.3	Watts
Pu	4996	g
Pu	87.6	wt. %
Aluminum	25	ug/g
Americium	55	ug/g
Bismuth	73	ug/g
Carbon	80	ug/g
Calcium	61	ug/g
Chloride	30	ug/g
Iron	37	ug/g
Fluoride	30	ug/g
Nitrate (water soluble)	390	ug/g
Silicon	140	ug/g
Uranium (238)	170	ug/g

Pressure behavior in Can 1, R200145

- Surveillance initiated on 12/13/01
- Gas analysis shows only He gas in first can after 437 days of surveillance, verified with GC, MS, Raman



1. Leak check at 1000 Torr
2. Lowered to RFETS pressure

GC sampling: - ΔP= -0.04 psi

Monitoring 3013 Storage Can 1 - PuO_2

Raman and GC results show only helium

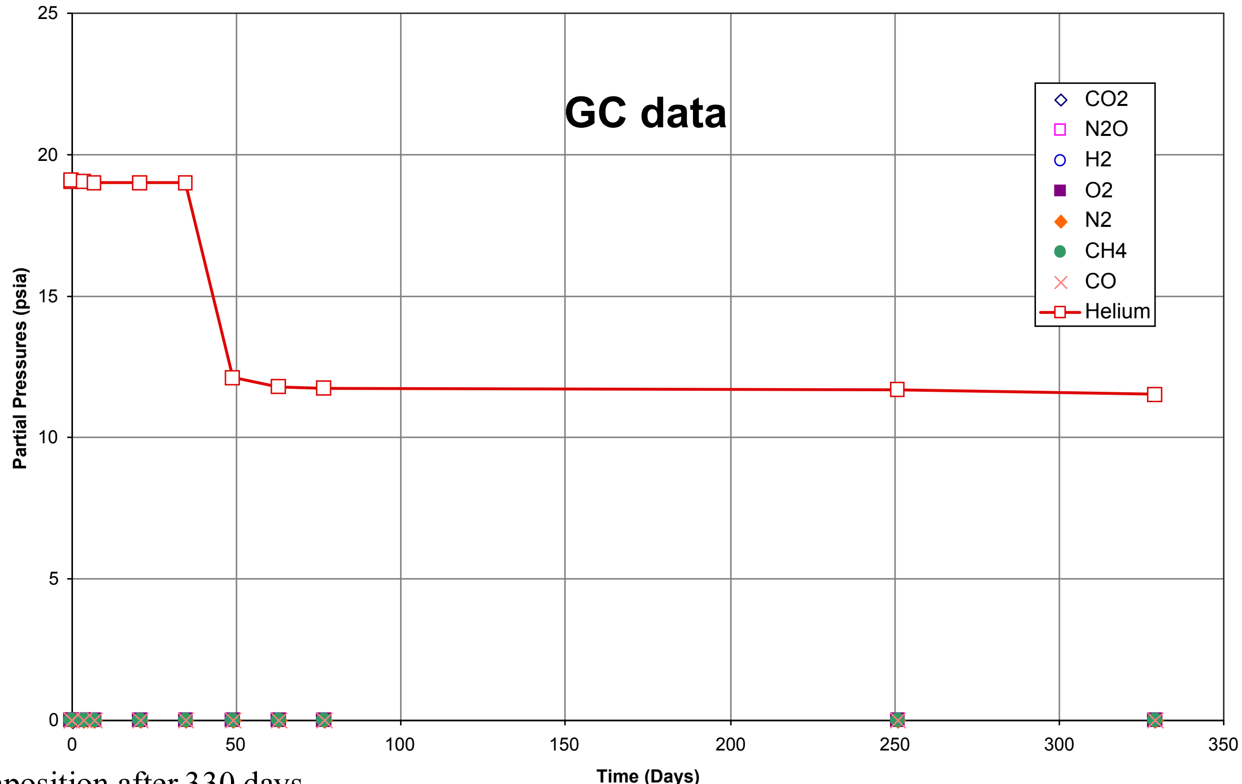


Table 1: 3013 storage can 1 headspace composition after 330 days, pressure is reported in psia.

Days	CO_2	N_2O	He	H_2	O_2	N_2	CH_4	CO
0.0	0	0	19.9	0	0	0	0	0
0.1	0	0	20.1	0	0	0	0	0
3.9	0	0	20.1	0	0	0	0	0
6.9	0	0	20.1	0	0	0	0	0
21.0	0	0	19.9	0	0	0	0	0
34.8	0	0	19.3	0	0	0	0	0
48.9	0	0	12.9	0	0	0	0	0
62.9	0	0	12.5	0	0	0	0	0
77.0	0	0	12.7	0	0	0	0	0
250.9	0	0	12.5	0	0	0	0	0
328.9	0	0	12.4	0	0	0	0	0

GC Data are corrected for

- temperature (average of can thermocouples).
- zero point drift of pressure gauge.

GC analysis is relative and multiplied by measured can pressure.

Monitoring of 3013 Storage Can 10 Calibration Gas

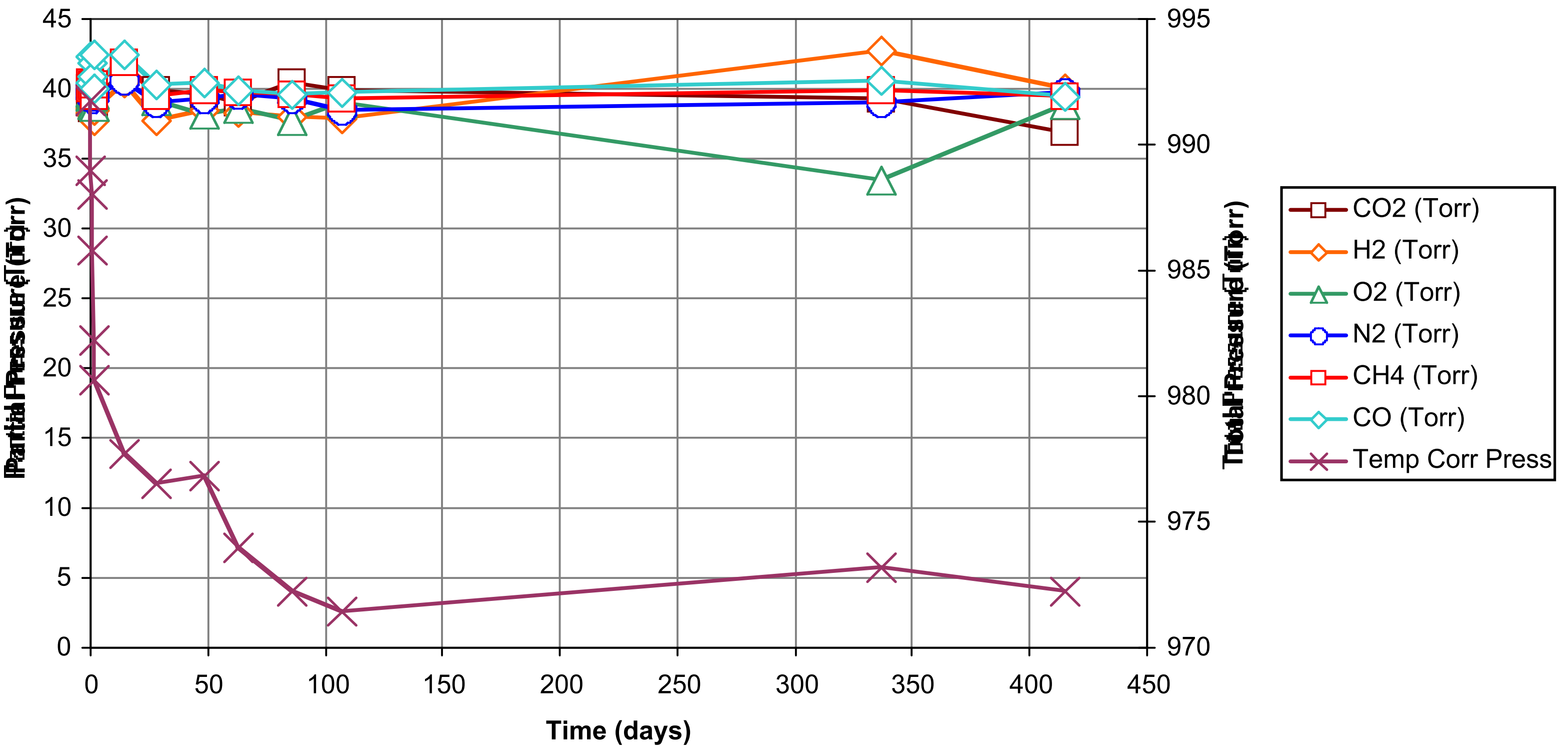
Purpose of Can 10:

- Reactivity of gases with walls.
- Sample procedure check.

•GC recalibration corrected scatter in GC data at 350 days.

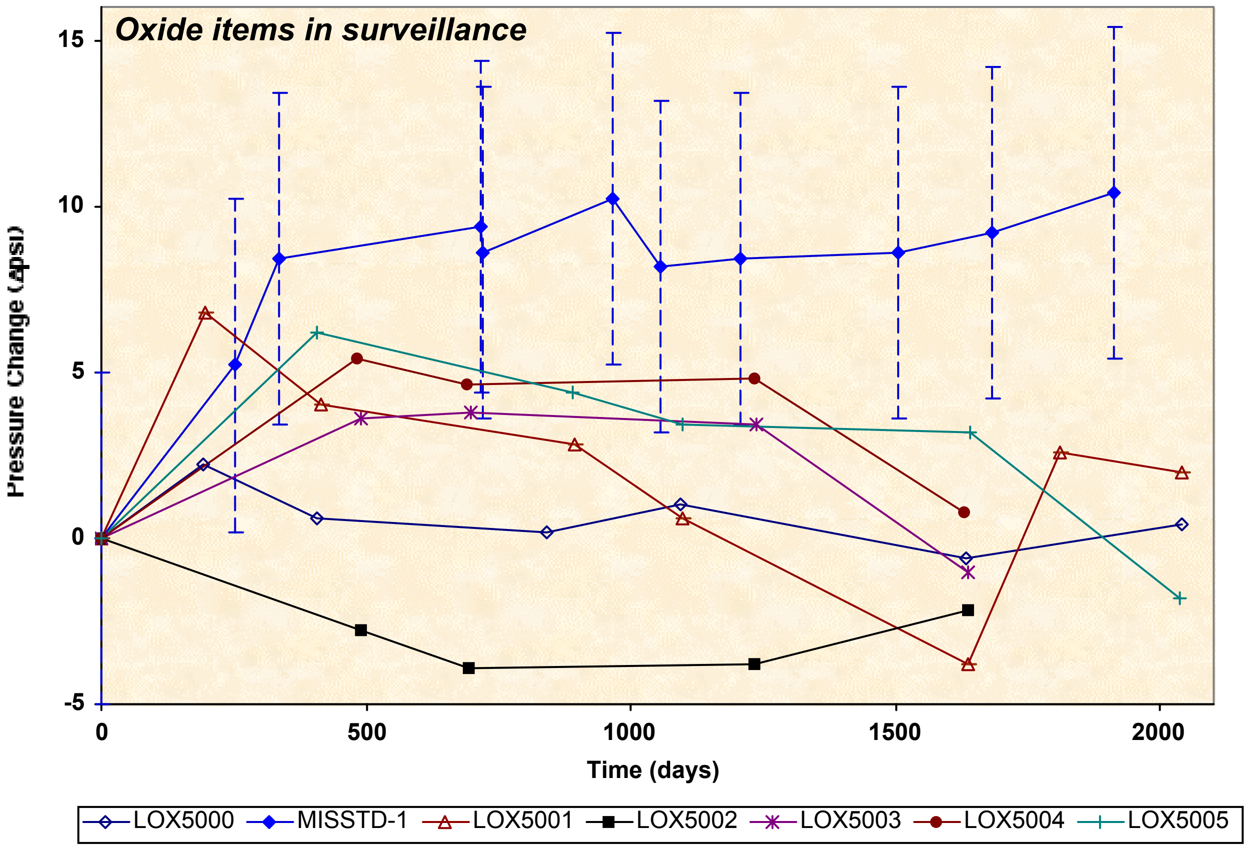
Change in composition is close to our limits of detection.

•Raman results are concurrent with GC data



Radiographic Surveillance of 3013 Containers with Bellows

- **Current surveillance includes 7 oxide containers (>85% Pu) and 14 metal containers (pure Pu) all packaged in He.**



Status

- **No metal items show Pu corrosion.**
- **All oxides have less than one monolayer of water equivalent.**
- **Most oxide pressure measurements fall within 2 sigma (5.6 psig)**
- **MISSTD-1 may have a 10 psig pressure increase.**

Large Scale Container Status

- Radiography of containers with bellows indicate no significant pressurization of containers
- Pressurization and evolution of polyatomic gases are not observed in first full scale oxide can
- CO_2 generation observed at higher temperature; Source of carbon is indeterminate
- Corrosion sensor data indicate low moisture and no occurrence of general corrosion
- H_2/O_2 issues: Graded AB approach will be taken for next 8 containers based on moisture levels; at least 2 containers will require a Readiness Assessment
- LA-14006: H_2 and O_2 concentration limits in large cans completed
- LA-UR-02-7356: 2002 Year End Report Completed
- Pu Futures Conference paper submitted

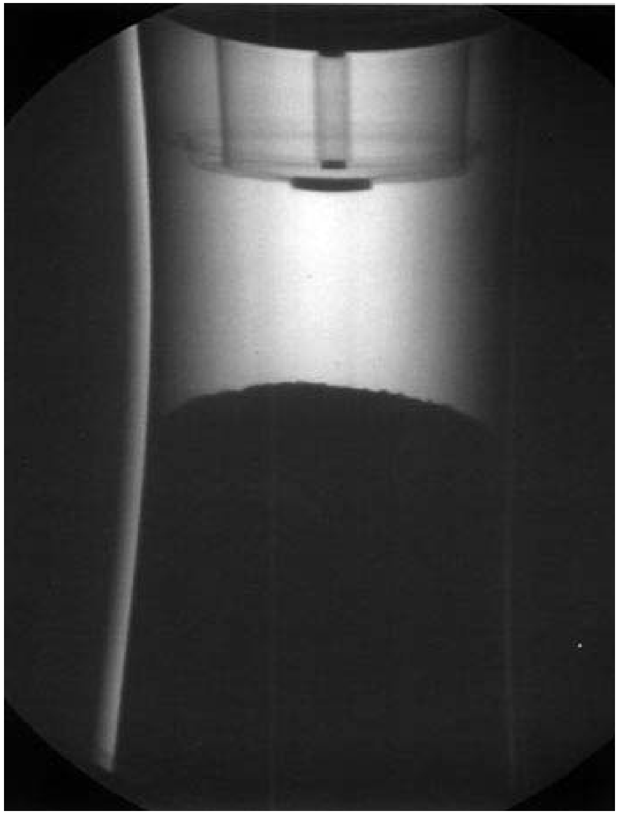
Supplemental Slides

Radiographic Surveillance of 3013 Containers with Bellows

- Current surveillance includes 7 oxide containers (>85% Pu) and 12 metal containers (pure Pu) all packaged in He.

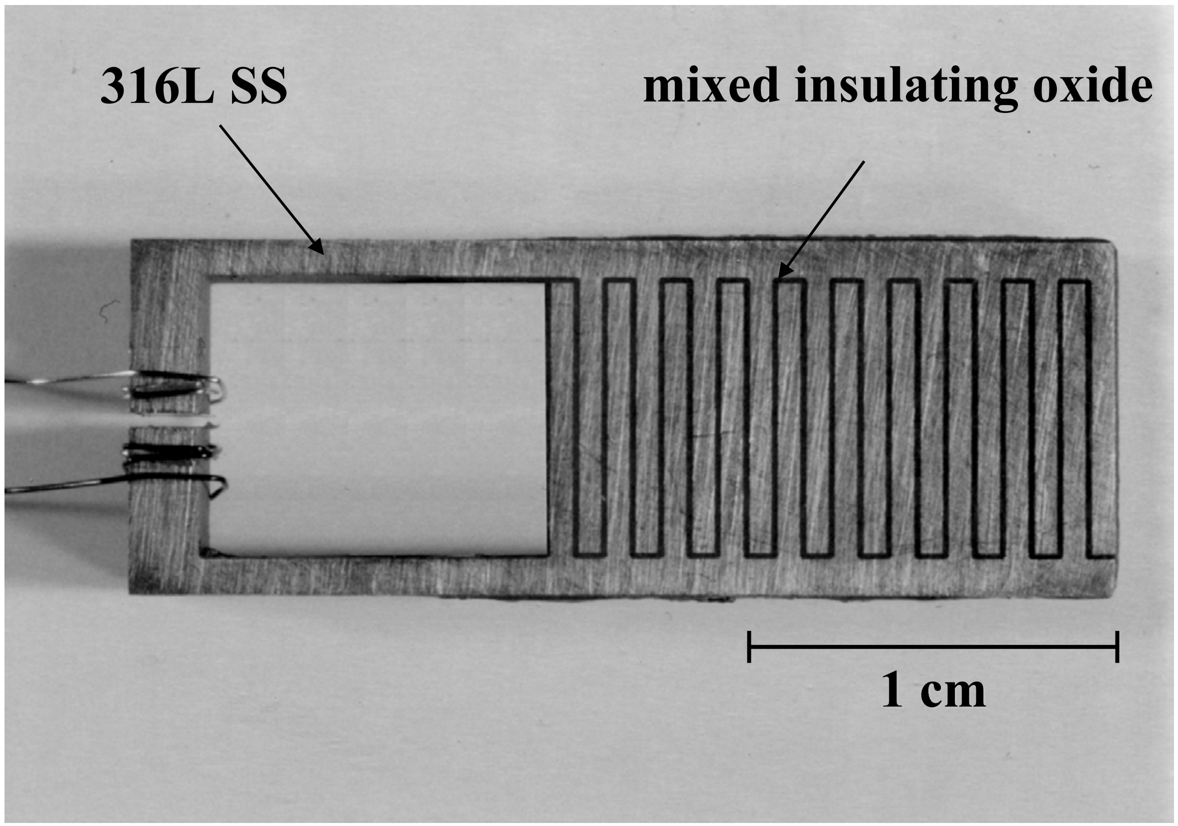
- Each item is inspected with radiography for signs of corrosion, oxide formation on the metal, and leakage.

- Bellows measurements are taken an a sign of internal pressurization.



Atmospheric corrosion rate monitor (ACRM)*

- ✧ Linear polarization resistance resistance (corrosion rate)
- ✧ Moisture content via electrochemical impedance spectroscopy



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